

## PRODUCTION OF ACTIVATED CARBONS FROM ILLINOIS COALS

Edwin J. Hippo AND William S. O'Brien  
Department of Mechanical Engineering and Energy Processes  
Southern Illinois University at Carbondale  
Carbondale, IL 62901-6603

Jian Sun  
Department of Civil Engineering  
University of Illinois  
Champaign, IL 61802

Keywords: Activated Carbons from Coal, Preoxidation, Surface Area of Chars

### INTRODUCTION

Although the predominant use of coal is for combustion applications, more beneficial, reasonable and profitable uses may be as a resource for the production of chemicals, and materials, including activated carbon. Activated carbons represent a family of carbonaceous substances manufactured by processes that develop the carbon's adsorptive properties (1). They are highly disorganized, aromatic lamellae which stack in 3-dimensional space to form porous solids (2-4). They normally have a high surface area, high adsorption capacities, and high surface reactivities. They are widely used in waste water treatment processes and are gaining increasing popularity for adsorbing vaporous organic molecules from gases and liquid phases. They are often the material of choice for many environmental applications and can also be used as a catalysts support.

Coals are a popular parent material for the production of activated carbons. Many workers have reported the production of high grade activated carbons from coal (5-17).

Several problems have kept coals from becoming dominant parent materials. One problem is the inherent mineral content of coals. Second, high and low rank coals are thermosetting solids which means that the microstructure of the activated carbon produced from these coals is relatively fixed. Only minor changes in microstructure can be made by controlling the weight loss during the activation process. This phenomena allows for consistency in the product but the quality of the product is not optimal. The opposite problem exists for bituminous coals. Bituminous coals melt during pyrolysis and the inherent pore structure collapses. The char must be heavily activated in order to produce a high grade of product. This can be circumvented by oxidation in air prior to the devolatilization step. However, the preoxidation step is difficult to control and the consistency of the end product is poor. Thus, bituminous coals give higher grade product than the lower or higher rank coals but the product consistency is poorer for the bituminous rank coals. Other chemical methods have also been used to prevent pore collapse. All of these processes are costly. Besides these problems, little is understood in terms of the basic fundamentals that produce a carbon of desired microstructure from a given parent coal. Thus, for a given feedstock many tests must be conducted to properly optimize both yield and product quality. This paper discusses the production of activated carbon from an Illinois coal with a two- and a three-step process.

### EXPERIMENTAL

The primary objective of this study was to demonstrate that an activated carbon with acceptable commercial properties could be made from a -20x100 mesh fraction of an Illinois Basin coal (IBC 106). This sample was chosen for its low ash yield and represents a major coal producing seam in Illinois. The analysis of the whole coal can be found elsewhere (18). Pretreatment time and temperature, devolatilization temperature, and activation time and temperature were studied as production variables. The carbon products were characterized by CO<sub>2</sub> single point BET, helium density, bulk density, pore volume, and a dynamic toluene adsorption test.

Figure 1 illustrates the three-step process for producing activated carbon from bituminous coal. Direct activation of two oxidized coals was also applied in order to reduce the total production time. The figure lists the various conditions for which samples were prepared.

The oxidation step for pretreating the raw coal was performed in an auto-programmable ashing furnace. Approximately 40 grams of coal sample was scattered as a 3 mm thick layer onto a 200 mesh sieve, and air was passed through the sieve screen at temperatures ranging from 150°C to 250°C.

The devolatilization and activation steps were carried out in a reaction system arranged as shown in Figure 2. The apparatus consists of a nitrogen and air supply system, a metering pump, a steam generating unit, a vertical reactor system, and a reaction flue gas cleanup unit. An annular sample basket was used in the experiment. To monitor the sample (reaction) temperature, a thermocouple (chromel-alumel) was inserted in the center of sample. Approximately 40 grams of preoxidized coal was used for each devolatilization step and 10 gm of char during each activation step. The air supply and the steam generating unit were used only during the activation reactions. The flow rate of nitrogen (for devolatilization) or steam, air and nitrogen mixture (for activation) were one liter/min.

A "Quantasorb" solids surface analyzer was used to measure the carbon surface area using carbon dioxide single point BET method (19). The helium density measurements were carried out in a "Stereopycnometer", as described by Lowell and Shields (19). The bulk density was calculated using the mass of an activated carbon sample and the volume of this sample measured in a 5 ml cylinder after 10 tapping times.

To evaluate the practical adsorption capacity of the products, a mini-column adsorption system was constructed as shown in Figure 3. A saturated toluene water mixture was pumped through the column. A data logger was used to record the percentage transmittance (%T), after passing the mixture through the column. The mini-column was made of stainless steel, about 8.7 cm in length, 3.5 mm I.D. and 6.35 mm O.D. Both ends of the column was plugged with a small wad of glass fiber to contain the sample. A charge of 0.2 gm of activated carbon was used for each test.

## RESULTS AND DISCUSSION

The first try at oxidation of the coal was carried out at 150°C following the studies reported by Maloney and Walker (9,10). The criterion for oxidation success was to treat the coal with air at 150°C until the coal lost its caking property (did not melt or agglomerate) during a 730°C heat treatment in a nitrogen atmosphere. An oxidation reaction at 150°C for 40 hours in flowing air converted the raw coal into the first non-caking, oxidized coal (CxOy 1). The coal gained 1.9 wt.% during this oxidation step. The oxidation temperature was then increased to 225°C and to 250°C, in an attempt to produce the oxidation treatment in a shorter time. The criterion for oxidation success was to oxidize the coal until it reached 1.9 wt.% weight gain (dry). The coal was weighed periodically. It took 6 hrs to reach the 1.9 wt.% gain target at 225°C and only 2 hours to reach the target at 250°C.

The 250°C reaction temperature was the highest on a practical basis, since the coal ignition temperature in this reactor was around 275°C (coal becoming ashed at 275°C in the furnace). The three oxidized coals (CxOy 1, CxOy 2, CxOy 3) were used for carbon production. The reactivity of the chars largely depends on the temperature of the char preparation step and the activation-gas composition. It was found in the earlier SIUC study [7] that a 1000°C devolatilization totally destroyed the original micropores in the unoxidized coal. Char devolatilized at 500°C seemed to be more reactive than the char devolatilized at 750°C. Since time of activation is an important economic factor, a more reactive char is desirable, provided that the char produces the desired quality of carbon.

In this work, Char 1 was gasified at 730°C to produce the first set of carbon products, C1/730/730. The rate of char weight loss is fast during the first several hours of reaction. Afterwards, the weight loss rate becomes linear. The carbon surface area develops gradually as the weight loss increases. The maximum surface area was reached at 60 hours, with a 63.73 wt.% weight loss. Activation for more than 60 hours resulted in a decrease in the surface area due to the destruction of the walls between micropores inside the particles.

The gasification temperature was increased to 780°C during the making of the second set of carbon products from Char 2. Both Char 2 and Char 1 were made from CxOy 1, while Char 2 was devolatilized at 500°C in an attempt to preserve the reactive sites in the char. The overall reaction rate at 780°C for Char 2 was much faster than that of Char 1 at 730°C. The maximum carbon surface area were reached after 17 hours of activation with a 70.93 wt.% weight loss. It is noticed in Figure 4 that the maximum surface areas in the production of C1/730/730 and C1/500/780 are not on the same point of char weight loss, because their gasification reactions were based on the different chars. But the surface area development is similar in both cases.

CxOy 2 was devolatilized at 500°C to make Char 3, on which activation tests at 780 to 880°C were performed. Surprisingly, regardless of the activation temperature, the maximum surface (about 1070 m<sup>2</sup>/g) developed at about 73% burnoff. At higher temperature, it became more difficult to obtain the target burnoff.

The specific surface areas were measured or calculated on a dry basis, which is conventionally used in industry. It is of interest to also calculate the carbon surface area on the basis of dry ash free (daf). In the production of C1/730/730, the value of the maximum surface area (1058 m<sup>2</sup>/g, dry) became 1464 m<sup>2</sup>/g (daf). The surface area value of the carbon after 96 hour activation jumped up from 872 m<sup>2</sup>/g (dry) to 1638 m<sup>2</sup>/g (daf).

The pore volume of a carbon adsorbent is one of the major factors that influence the carbon adsorption behavior. This property should normally increase step by step as more and more surface area is developed while the coal converts to form porous carbon. As a result, the carbon bulk or apparent density should decrease, and the helium (or true) density should increase. Figure 5 illustrates the change of pore volume during the gasification step.

The measurement of each carbon's capacity for toluene adsorption was the major method used in this study to evaluate the applied performance of the carbon adsorbents. These experiments were run in a mini-column adsorption system. Toluene is considered as a practical adsorbate which represents potential industrial solvents and domestic organic pollutants.

A UV spectrophotometer was used to monitor the percentage transmittance of the effluent stream coming from the column, yielding a time history of percentage transmittance of the flow stream. The toluene adsorption capacities of all the carbon products produced in this work are summarized in Table 1.

Darco coconut charcoal (Fisher Scientific), a commercial activated carbon, was chosen as the reference adsorbent for this study. The "raw" adsorbent with an "as-received" commercial size (-6+14 mesh) demonstrates very poor adsorption behavior, probably because of the small ratio of particle diameter to tube diameter. The commercial carbon was then ground into the -20+100 mesh size-range, the same as that of the coal-carbons made during this study, in order to reduce

the diffusion distance and improve the adsorption efficiency.

The toluene "adsorption capacity" of the carbon is defined as the amount of toluene removed from the water stream by each gram of carbon. The adsorption capacity in this study is defined by the amount of toluene adsorbed before the 5% level (break point) was reached on the breakthrough curve. It took 200 minutes for the concentration ratio to reach the break point with the C1/730/730 carbon, which is about 140 minutes longer than with the commercial carbon.

The C1/500/780 carbon shows the highest adsorption capacity (1.57 g/g) that is consistent with its highest surface area. The C2/500/780 carbon also demonstrates a very high adsorption capacity, only second to the C1/500/780 carbon. While the C2/500/800, C2/500/840, and C2/500/860 carbons have about same high surface area values as the C2/500/780 carbon, they exhibit smaller adsorption capacities.

In consideration of the mass diffusion behavior during adsorption, the C1/500/780 and C2/500/780 carbons may have a size-range of micropores that would cause slower toluene mass transfer inside carbon particles. This is depicted by the small slopes of the respective breakthrough curves. Another two products, the C2/None/860 and C3/None/860 carbon, made by direct gasification at 860°C on oxidized coals were also produced. They demonstrated quite similar adsorption behavior to that of carbon made by char gasification at the same temperature.

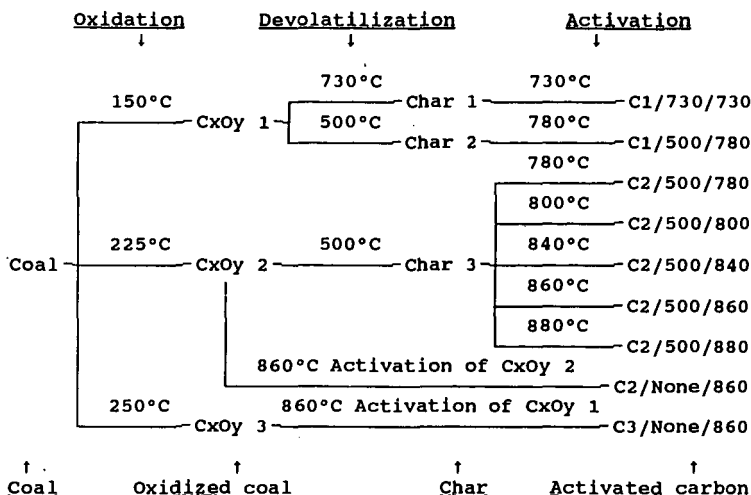
## CONCLUSIONS

It can be concluded from the results of this study that activated carbon adsorbents with acceptable commercial properties can be produced from an Illinois Basin coal. A total of nine carbon products were produced, seven of these having carbon dioxide specific surface area greater than 1000 m<sup>2</sup>/g (dry), as compared with the surface area of 547 m<sup>2</sup>/g (dry) measured for a commercial activated coconut carbon. All the SIUC products demonstrated better toluene adsorption. The adsorption capacity of the carbon with the largest pore surface area of 1114 m<sup>2</sup>/g (dry), corresponding to 1560 m<sup>2</sup>/g (daf), is four times greater than that of commercial carbon. The highest daf surface area value was 1638 m<sup>2</sup>/g, corresponding to 872 m<sup>2</sup>/g (dry). Devolatilization at lower temperatures is preferred for the conservation of the reactivity of resultant char. The successful production of carbons by direct gasification on oxidized coals indicates that the devolatilization process might be ignored if the oxidized

There have been three pretreatment oxidation temperatures tested in this study. Oxidation at 150°C probably takes too long (40 hours) to be practical in industry. Oxidation at 250°C seems to be too strong, causing partial damage of aromatic structure of the carbon. The oxidation pretreatment at 225°C seems to be the most feasible oxidation temperature of those evaluated in this study.

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### Reaction

### Condition

Oxidation

oxidized at 150, 225, or 250°C in flowing air with unlimited supply for 40, 6 and 2 hours.

Devolatilization

devolatilized at 500 or 730°C in nitrogen for 1 hour.

Activation

activated (gasified) at 730-880°C in 45% steam, 4% oxygen in nitrogen for 3-96 hours.

Figure 1. Production Procedures for Making Activated Carbon from IBC-106 Coal

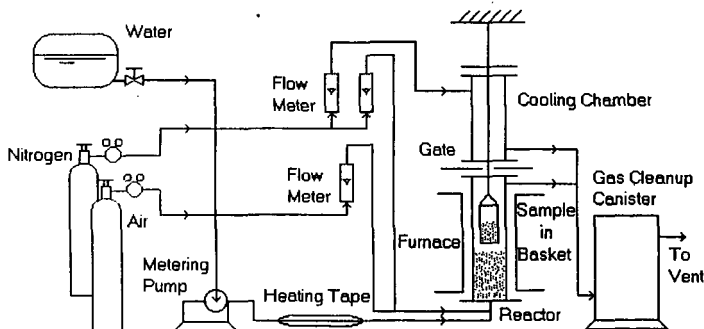


Figure 2. Vertical Tube Furnace Reactor System

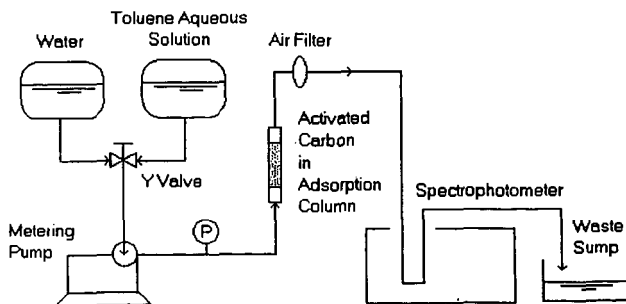


Figure 3. Mini-Column Adsorption System

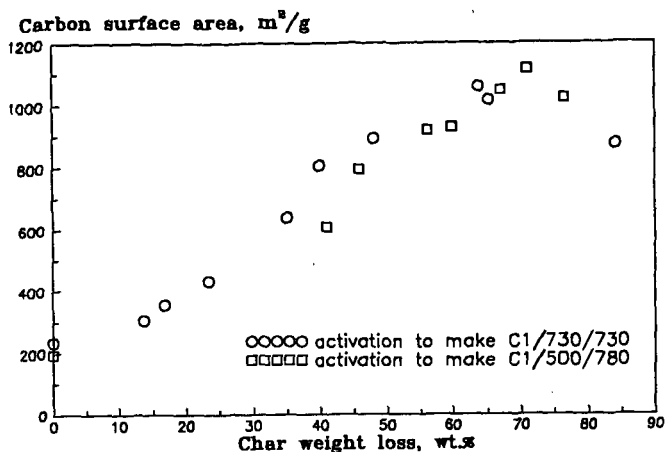


Figure 4: Relationship Between Surface Area and Weight Loss

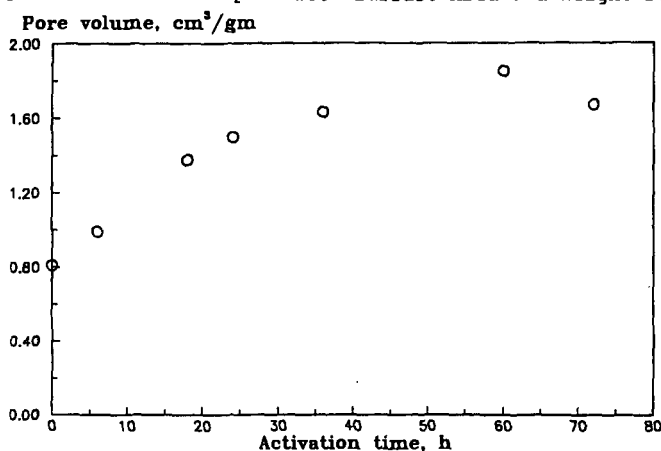


Figure 5: Pore Volume Develops During Activation

TABLE 1  
 TOLUENE ADSORPTION CAPACITIES OF CARBONS  
 WITH MAXIMUM SURFACE AREA

Carbon	Carbon surface area m <sup>2</sup> /g	Toluene adsorption capacity g/g
Darco	547	0.31
C1/730/730	1058	1.05
C1/500/780	1114	1.57
C2/500/780	1054	1.36
C2/500/800	1076	1.00
C2/500/840	1031	0.74
C2/500/860	1050	0.89
C2/500/880	968	0.89
C2/None/860	1040	0.84
C3/None/860	852	0.84